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RESEARCH ARTICLE

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Partitioning of heavy metals during municipal solid waste incineration on a laboratory fluid bed furnace

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Abstract The content of heavy metals in the main physical compositions of municipal solid waste (MSW) is analyzed. The effects of temperature, chlorine and water on the partitioning of heavy metals are studied using a laboratory fluidized-bed (FB) furnace with simulated MSW composition. The experimental results show that temperature and chloride content in the feed have significant influence on the volatility of heavy metals, especially those of lower boiling point such as Hg, Cd and Zn. The influence of water is slight.

Keywords heavy metal, municipal solid waste incineration, transfer

1 Introduction

With the development of the economy, the amount of municipal solid waste (MSW) has been increasing and the composition of MSW changing significantly. The organism and the heat value provide essential preconditions for MSW incineration (MSWI) because they take on an increasing trend in MSW. The MSWI has advantages that include high speed of disposal, high ratio of the volume reduction, high ratio of mass reduction, reuse of energy, occupancy of a small little area and high degree of harmlessness. As a result, MSWI projects are being developed rapidly, especially in the developed coastal areas in China.

Due to the complex composition of MSW, heavy metals contained therein may transform during MSWI and are finally distributed in gas, fly ash and slag. With recognition of the toxic characteristics of heavy metals, pollution caused by these metals in MSWI has become a new research field.

In resent years, aiming at the discovery of transferring characteristics of heavy metals in MSW, some scholars abroad pointed out that the release of heavy metals during MSWI is related not only to the percentage of heavy metals in MSW, but also to incineration temperature and reaction with the nonmetal component such as chlorine [1]. In China, the research on MSW was conducted very late, and research on the transferring mechanism of heavy metals is especially limited [2–4]. Because of different living standards and ways of collecting waste (done separately abroad), the composition of MSW at home is obviously different from that abroad. Domestic MSW comprises of complex components (almost everything) and a lot of water. Therefore, in dealing with this kind of MSW, it is necessary to study the transferring characteristics of heavy metals during MSWI.

In this paper, the percentage of heavy metals in typical MSW is analyzed, and the components of MSW are simulated. The effect of incineration temperature, chlorine content and water on the transferring characteristics of heavy metals is studied using fluidized-bed (FB).

2 Collection of waste sample and composition of simulated MSW

Because of the difference in lifestyles, seasons and living areas, the percentage of components in MSW is evidently different in various cities. Furthermore, due to the complexity of the waste, it is hard to analyze all the components. In the experiment, more than ten kinds of typical waste components are collected, and heavy metal content is tested. The result is shown in Table 1.

In the waste incineration experiments, the samples are collected according to components of Chinese MSW as shown in Table 2 [5]. The waste components are shown in Table 3. Alkaline battery is not considered in the simulated MSW composition although it is high in mercury content, because there are few alkaline batteries in the garbage.

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Table 1 Content of heavy metals in the main physical compositions of MSW(dry basis) (mg/kg)

Waste kind	Paper				Plastic			Rubber
	Newspaper	Food packaging	Chipboard	Others	Color plastic bag	White	Transparence	
Hg	0.007	–	0.020	0.012	0.039	0.061	0.056	0.013
Cr	4.021	16.187	6.534	4.471	104.58	4.801	5.573	36.559
Ni	2.011	4.439	1.647	1.297	26.337	1.199	0.467	16.080
Cd	0.084	–	–	–	0.220	–	–	2.551
Zn	22.488	31.576	58.593	22.735	67.398	20.026	20.827	25 948.1
Pb	3.635	11.269	26.151	6.812	240.125	6.629	–	28.766
Cu	19.998	15.621	10.900	–	96.664	3.985	–	0.954

Waste kind	Cabinet rest	Courtyard waste				Fabric	Alkaline battery	Glass
		Leaves	Weed	Wood scraps	Dust			
Hg	0.000 8	0.000 6	0.005	0.007	0.038	0.061	0.876	0.001 2
Cr	0.352	8.556	19.022	19.361	12.106	32.011	0.01	0.489
Ni	0.934	3.251	7.887	9.486	4.862	3.656	–	–
Cd	–	0.312	0.316	0.351	0.453	0.125	0.256	0.081
Zn	57.420	32.326	46.994	32.967	56.746	122.128	–	–
Pb	–	9.247	5.857	1.239	20.873	13.532	0.02	1.032
Cu	–	1.462	3.428	1.155	2.314	0.476	–	–

Table 2 Main composition of MSW in China

Kitchen waste	Waste paper	Fibre	Bamboo and wood	Plastics	Scrap metal	Glass and porcelain	Coal ash and tile	Others
52.00	4.90	1.18	1.08	11.2	1.28	4.09	20.64	3.00

Note: Others refer to a mixture of weed, sawdust, leaves, etc.

Table 3 Composition of simulated MSW (%)

Kitchen waste	Newspaper	Other paper	Fabric	Plastics and rubber	Dust	Others
45	6	3	3	8	30	5

Note: Others refer to a mixture of weed, sawdust, leaves, etc.

3 Experimental setup and analysis and testing methods

3.1 Experimental setup

The FB experiment setup, which is composed of an FB reactor and a flue gas absorption section, is shown in Fig. 1. The inner part of the FB is a screw thread porcelain pipe with a height of 500 mm and an inner diameter of 40 mm. The air distribution plate is a stainless steel grid with many apertures of about 50 μm. Inside the bed layer, a K-type thermocouple to test the bed temperature is installed. The air distribution system is made up of a centrifugal blower and a rotor flowmeter. Quartz sand is chosen as bed material. According to Table 3, the simulated MSW is put in the boiler respectively through the throw-material-orifice at the upper part of the bed. The gas absorption section, made up of four absorption bottles, is referred to the EPA METHOD 101. The former two bottles, which contain $5\%HNO_3 + 10\%H_2O_2$, are used to absorb ionic heavy metals. The latter two bottles, which contain acidification $KMnO_4$ solution, are used to absorb elementoid heavy metals.

3.2 Analysis and testing methods

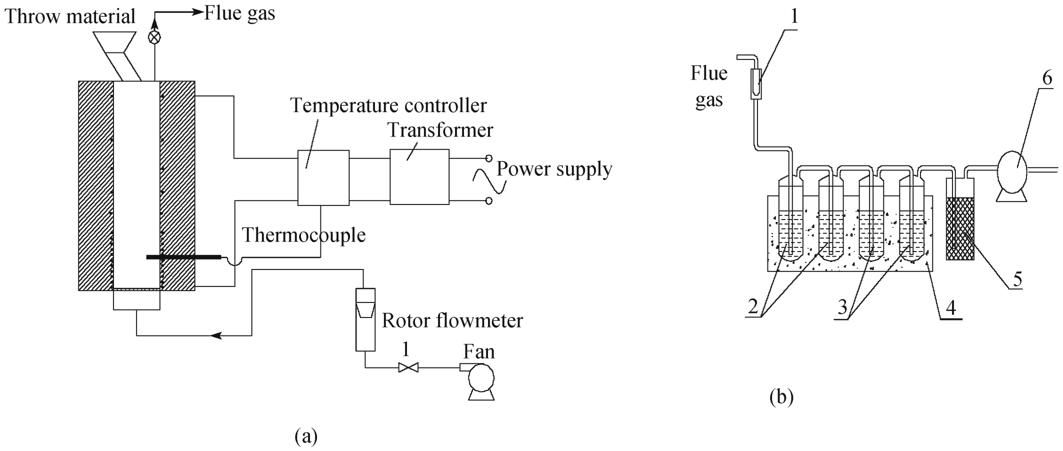
In the experiment, according to USEPA METHOD 3050 [6], the typical MSW components are digested by using the HNO_3-HF-$HClO_4$ method, and then heavy metal content is tested. The flue gas absorption is referred to EPA METHOD 29.

Mercury in the digestion solution and the absorption solution is tested by a cold atomic fluorescence instrument. Other heavy metals such as Cu, Zn, Pb, Cd, Cr, and Ni are tested by atomic absorption spectroscopy (model: UNICAM 969).

4 Results and analyses

4.1 Heavy metal contents in MSW components

As shown in Table 1, heavy metal content such as Zn, Pb, Cr, and Cu is higher than that of Ni, Cd, and Hg in MSW components, and every MSW component that is collected contains some heavy metals to a certain extent. Among MSW components, color plastics, rubber, fabric and dust have higher heavy metal content. Cr content is the highest in color plastics, which is over 20 times that of colorless and transparent plastics and obviously higher than other MSW components. Cr content is also high in rubber. Pb content is



(a)

(b)

Fig. 1 Experiment setup
1) Filter; 2) 5% $HNO_3 + 10\%\ H_2O_2$; 3) 4%$KMnO_4 + 10\%H_2SO_4$; 4) ice bath; 5) silica gel; 6) pump

highest in color plastics and then in chipboard, rubber and dust, which is about 20–30 mg/kg, but is less in other MSW components. Of the seven heavy metals, Zn content is high in all MSW components, especially in rubber reaching 25 948.1 mg/kg, which is ten times or more than 100 times that of other MSW components. Cd content is high in rubber but low in other MSW components. Ni and Cr contents are very similar in all kinds of MSW components, are highest in color plastics, and not so high in other MSW components. Heavy metals contents obtained from simulated MSW digestion are summarized in Table 4.

Table 4 Content of heavy metals in simulated MSW mg/kg

Pb	Cd	Cu	Zn	Ni	Cr	Hg
30.663	0.213	11.803	833.739	5.236	15.858	0.015

4.2 Effect of temperature on volatilization characteristics of heavy metals

The volatilization characteristics of seven heavy metals are studied at different temperatures from 500 °C to 900 °C as shown in Fig. 2. The experimental results show that the effect of temperature on those characteristics of heavy metals is different. The effect of temperature change on the volatilization characteristics of Hg and Cd is obvious, but that of Pb, Zn and Cu is not so obvious. The effect of temperature change on the volatilization characteristics of Cr and Ni is the least. When at low temperature (about 500 °C), only Pb, Cd and Zn have little volatilization, while other heavy metals have almost no volatilization.

From the experiment it is found that the volatilization ability of Hg is much higher than that of six other heavy metals at low temperature. The volatilizations of Pb and Zn are similar. At a temperature of about 700 °C, they have an evident volatilization ability. Ni and Cr have obvious volatilization ability above 800 °C. Figure 3 shows that temperature change has a great effect on metal vapor pressure, which increases with an increase in temperature, and the vapor quantity of heavy metals also increases with a rise in temperature [7]. Figure 3 also shows that the vapor pressures

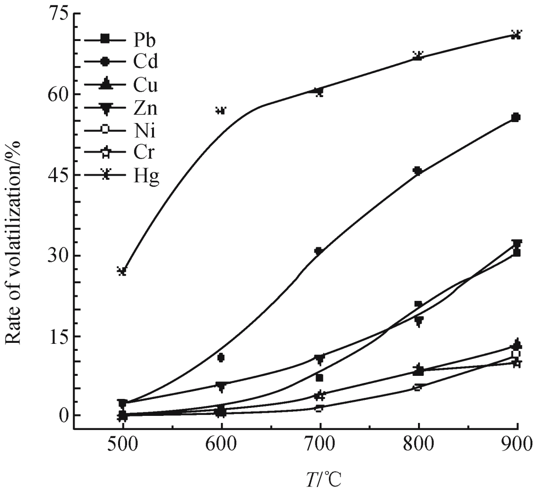


Fig. 2 Effect of temperature on the partitioning of heavy metals

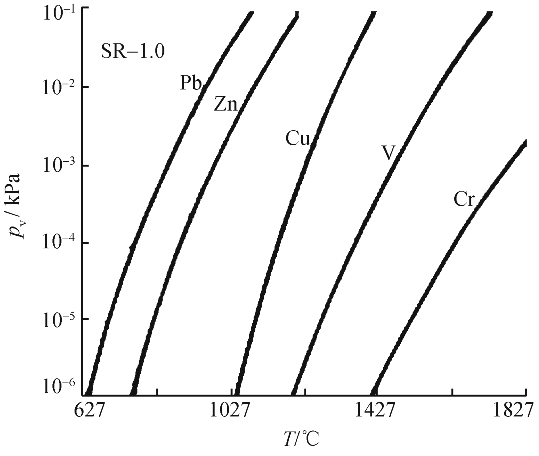


Fig. 3 Effect of temperature on the evaporating pressure of heavy metals

for various metals have great differences, and all the metal vapor pressures are very low (less than 1×10^{-6} atm). This basically supports the experimental conclusion, except the fact that the evaporation characteristics of Pb and Zn are different from the regulation obtained from Fig. 3, which may be caused by experimental error. The evaporation ratios of Pb and Zn are very close. Of all the heavy metals studied, Hg is the most likely to vaporize, Cd is the second, Pb and Zn are the next, and Cr and Ni are the least likely to vaporize, which confirms the conclusion of Wang [8].

4.3 Effect of chlorine on partitioning characteristics of heavy metals

In the experiment, organic and inorganic chlorine are used at temperatures of 600 °C and 900 °C respectively to study chlorine mixture and its effect on the characteristics of heavy metals. The amount of chlorine accounts for 5% of MSW.

Figures 4 and 5 show that the volatility of heavy metals increases with an increase in either organic chlorine or inorganic chlorine, and the effect of organic chlorine is greater than that of inorganic chlorine, namely the effect of PVCs is greater than that of NaCl. The higher the temperature, the more the volatilization quantity of heavy metals is. The existence of chlorine obviously affects the content of Pb, Zn, and Cd in the flue gas, but chlorine mixture has less effect on Cr and Cu. Chlorine mixture also has a greater effect on the volatile and half-volatile status of heavy metals, but has less effect on involatile or difficult volatile heavy metals.

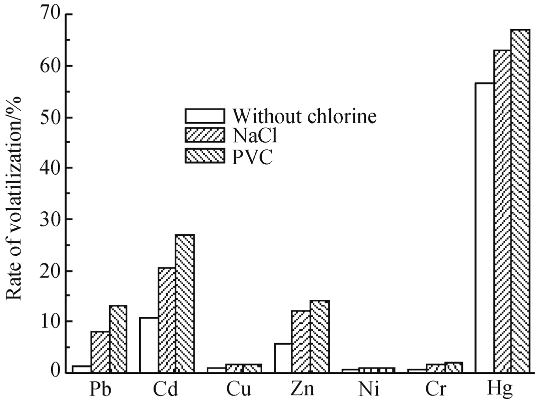


Fig. 4 Effect of chlorine under 600 °C

Based on the experimental results above, the mechanism can be summarized as follows. During the MSWI process, heavy metals will vaporize to a certain degree at the high temperature, and gradually condense with the decrease of flue gas temperature. Because of the reaction of chlorine with heavy metals, heavy metal chloride is generated. The vapor pressure of heavy metals in chloride status is higher than that in oxide status, increasing the volatilization quantity of heavy metals. Chlorine mixture delays the process of coagulation of heavy metals and decreases the dew-point temperature [9]. The bonding force between NaCl is larger than that between PVC, increasing the likelihood that PVC will decompose and Cl^- will increase [6]. Adding PVC will thus affect a greater increase in heavy metal volatilization quantity than adding NaCl. Moreover, the higher the incineration temperature, the more obvious the regulation is. A high incineration temperature is more apt to increase the volatilization quantity of heavy metal and its chloride, i.e. under the temperature of 900 °C, it is easier for heavy metals to vaporize than under the temperature of 600 °C.

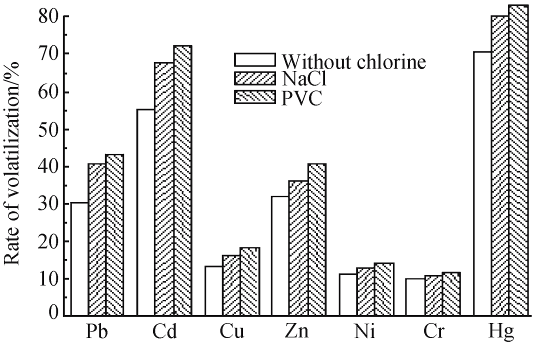


Fig. 5 Effect of chlorine under 900 °C

In recent years, and with changing MSW components, plastics are taking on an increasing trend, and chlorine in MSW incinerator is also increasing. The high chlorine content and its effect on heavy metal transferring characteristics in MSWI are further studied. The mixture rates of PVC in simulated MSW are 5% and 10%, and the incineration temperature is 900 °C. The result is shown in Fig. 6.

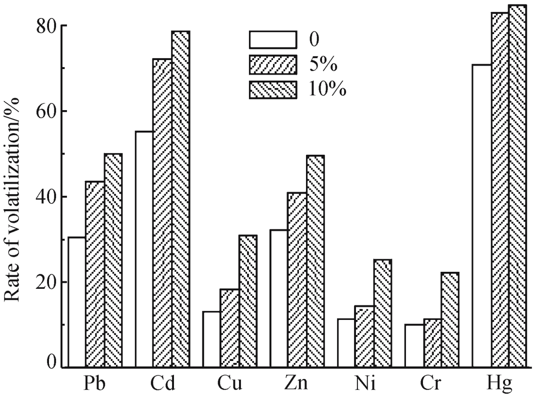


Fig. 6 Partitioning of heavy metals with different chlorine content

It can be seen that with the increase in chlorine content, the evaporation quantity of heavy metals takes on an increasing trend. When chlorine content is low, the volatilization quantity of volatile and half-volatile heavy metals such as Cd, Hg, Pb and Zn increases obviously, but that of difficult volatile heavy metals such as Cu and Ni do not increase as much. When chlorine content reaches a certain degree, the volatilization quantity of difficult volatile heavy metals also increases. It can be concluded that chlorine has a significantly positive effect on heavy metal volatilization characteristics and on difficult volatile heavy metals in high chlorine content.

4.4 Effect of water on partitioning characteristics of heavy metals

The mixed MSW components after torrefaction are adopted in the above experiment. Because the water content is high in real MSW (about 40%–50%), some water is added into the mixed MSW components after torrefaction. Under the temperature of 900 °C, the effect of water on partitioning characteristics of heavy metals in the process of incineration is studied. The result is shown in Fig. 7.

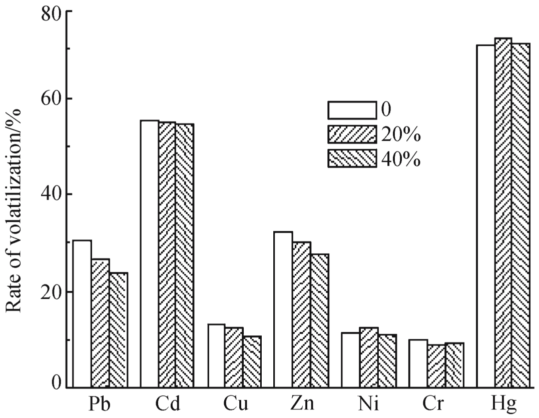


Fig. 7 Heavy metals' partitioning with different water content

It can be seen that when the water content increases, the volatilization characteristics of heavy metals take on a decreasing trend, although the effect is not highly remarkable. The vapors of Zn and Pb decrease more obviously than others. When the water content reaches 0%, 20%, and 40%, the evaporation rate of Pb reaches 30.32%, 26.4%, and 23.8% respectively, and that of Zn reaches 32.2%, 30%, and 27.6%. The change of water content has little effect on Cu and has almost no effect on Hg, Cd, Ni, and Cr.

In the process of MSWI, the volatilization of heavy metals is not only connected with the incineration temperature, but also more closely related to the existence of chlorine at incineration atmosphere. Chemical reaction occurs in heavy metals and in chlorine, and heavy metal chlorides are produced and increase the volatilization quantity of heavy metals. In the case of Pb, when there is water in MSW components, the following reactions will occur

$$\mathrm{Pb} + \mathrm{Cl} \Leftrightarrow \mathrm{PbCl}$$

$$\mathrm{PbCl} + \mathrm{Cl} \Leftrightarrow \mathrm{PbCl_2}$$

$$\mathrm{PbCl} + \mathrm{H_2O} \Leftrightarrow \mathrm{PbO} + \mathrm{HCl}$$

Because the existence of water turns metal chloride into metal oxide, the volatilization quantity of heavy metals such as Pb, Zn, Cu decreases. However, the case for Hg and Cd can be explained in the following manners. First, because both Hg and Cd are always in elementoid status, the existence of water at incineration atmosphere has little effect. Second, the volatility of the chemical form (chloride form and oxide form) of these two elements is high. Under high temperature, water has little effect on the volatilization characteristics. Ni and Cr often take on the oxide form, the content of chloride is minimal and the volatilization quantity is very low. Therefore, according to the equations above, the existence of water has no great effect on the volatilization characteristics of such heavy metals. The fact that the increase in water increases the volatilization quantity of other parts of heavy metals may be caused by experimental error.

5 Conclusion

When analyzing the MSW components, a certain number of heavy metals were found in all MSW components. Of the seven heavy metals studied, Zn content was the highest, that of Pb was second, and the contents of Cd and Hg were the least. The contents of heavy metals in color plastics, rubber, weed and dust were all high for the 18 kinds of MSW components studied.

The MSWI experimental results show that the incineration temperature has a certain effect on transferring characteristics of heavy metals, especially on volatile heavy metals. The existence of chlorine increases heavy metal volatilization quantity. The more chlorine content, the greater the effect is. The existence of water in the incineration process makes some of the heavy metals, such as Pb and Zn, take on a decreasing trend, but has little effect on other heavy metals. Cd and Hg have similar transferring characteristics, namely the evaporation of Cd and Hg finally occurs in the fly ash, and there is little content in the slag. This is especially true for Hg. Both Pb and Zn are finally distributed in the fly ash and slag. Ni, Cr and Cu have similar distributing regulations, and are mainly distributed in the slag.

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